

1,091,197

PATENT SPECIFICATION



NO DRAWINGS

1,091,197

Date of Application and filing Complete Specification: April 26, 1965.

No. 17475/65.

Application made in United States of America (No. 366,136) on May 8, 1964.

Complete Specification Published: Nov. 15, 1967.

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SPECIFICATION NO. 1,091,197

By a direction given under Section 17 (1) of the Patents Act 1949 this application proceeded in the name of KEWANEE OIL COMPANY, a Corporation organized and existing under the laws of the State of Delaware, United States of America, of P.O. Box 591, Bryn Mawr, State of Pennsylvania, United States of America.

THE PATENT OFFICE

D 104309/8

to us, and the method by which it is to be performed to be particularly described in and by the following statement:—

This invention relates generally to the electro-deposition of bright nickel plate substantially free of imperfections such as skip defects and missed areas. More particularly, this invention relates to the use of minute or small amounts of an unsaturated carboxylic acid, the corresponding esters or the corresponding amides thereof to overcome skip or misplate in an acid nickel plating bath containing active acetylenic brighteners or other unsaturated brighteners.

The acetylenic brighteners and the other brighteners depending on unsaturation to effect brightening of nickel plate have been difficult to employ because of their strong activity; they frequently exhibit excellent brightening characteristics but are not commercially acceptable because they cause misplating in the recessed areas or areas of low current density on the article to be plated. With the advent of acetylenic brighteners, numerous compounds containing triple bonds and/or double bonds have been tested and studied for their properties as brighteners. The majority of the sufficiently water soluble compounds were found to impart at least some brightening effect to a plating bath, the effect ranging from slight to strong with pronounced "skip" or misplating.

As is well known to those skilled in the art there is no difficulty in finding unsaturated compounds having brightening activity. Most of the unsaturated compounds manifesting activity as brighteners are apparently too active; they have a detrimental effect on the surface of the article to be plated which often takes the form of "skip" or misplate in areas of low current density. The phenomenon of [Price 456d].

problem of misplating caused from the use of the more active acetylenic brightness by adding small amounts of compounds which act as tempering agents supposed counteracting the strong absorption properties of the brighteners.

Certain classes of compounds have been shown to act cooperatively with the unsaturated brighteners to overcome misplating and permit the use of a wide range of current densities (2 amperes per square foot to over 100 amperes per square foot) such as those demanded by commercially bright nickel processes. It has been found, however, that the classes or types of compounds having the properties desirable for overcoming misplating frequently are undesirable because they are detrimental in other respects; the leveling characteristics of the bath are affected and/or the deposits have poor ductility, being brittle usually with sections of high stress.

The invention consists in a bath for electro-depositing bright nickel free of misplating comprising an aqueous solution of:

(A) at least one nickel salt;
(B) a brightener containing an acetylenic group;
(C) a sulfo-oxygen carrier;
and characterized by the presence therein of
(D) a water-soluble unsaturated tempering agent adapted to prevent misplating comprising a carboxylic acid, ester thereof or amide thereof, having one of the following nuclei

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(a) —C≡C—

(b) —C=| | | C=C—

SPECIFICATION AMENDED - SEE ATTACHED SLIP

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Index at acceptance:—C7 B(1R, 1T)

Int. Cl.—C 23 b 5/08

COMPLETE SPECIFICATION

Electrodeposition of Bright Nickel

We, THE HARSHAW CHEMICAL COMPANY, a corporation organized and existing under the laws of the State of Ohio, United States of America, located at 1945 East 97th Street, Cleveland 6, State of Ohio, United States of America, do hereby declare the invention for which we pray that a patent may be granted to us, and the method by which it is to be performed to be particularly described in and by the following statement:

This invention relates generally to the electrodeposition of bright nickel plate substantially free of imperfections such as skip defects and missed areas. More particularly, this invention relates to the use of minute or small amounts of an unsaturated carboxylic acid, the corresponding esters or the corresponding amides thereof to overcome skip or misplate in an acid nickel plating bath containing active acetylenic brighteners or other unsaturated brighteners.

The acetylenic brighteners and the other brighteners depending on unsaturation to effect brightening of nickel plate have been difficult to employ because of their strong activity; they frequently exhibit excellent brightening characteristics but are not commercially acceptable because they cause misplating in the recessed areas or areas of low current density on the article to be plated. With the advent of acetylenic brighteners, numerous compounds containing triple bonds and/or double bonds have been tested and studied for their properties as brighteners. The majority of the sufficiently water soluble compounds were found to impart at least some brightening effect to a plating bath, the effect ranging from slight to strong with pronounced "skip" or misplating.

As is well known to those skilled in the art there is no difficulty in finding unsaturated compounds having brightening activity. Most of the unsaturated compounds manifesting activity as brighteners are apparently too active; they have a detrimental effect on the surface of the article to be plated which often takes the form of "skip" or misplate in areas of low current density. The phenomenon of

skipping or misplating the areas of low current density is presumed to be the result of either excessive absorption or a special type of adsorption of the unsaturated compounds particularly those compounds containing a triple bond.

There have been attempts to overcome the problem of misplating caused from the use of the more active acetylenic brightness by adding small amounts of compounds which act as tempering agents supposedly counteracting the strong absorption properties of the brighteners.

Certain classes of compounds have been shown to act cooperatively with the unsaturated brighteners to overcome misplating and permit the use of a wide range of current densities (2 amperes per square foot to over 100 amperes per square foot) such as those demanded by commercially bright nickel processes. It has been found, however, that the classes or types of compounds having the properties desirable for overcoming misplating frequently are undesirable because they are detrimental in other respects; the leveling characteristics of the bath are affected and/or the deposits have poor ductility, being brittle usually with sections of high stress.

The invention consists in a bath for electrodepositing bright nickel free of misplating comprising an aqueous solution of:

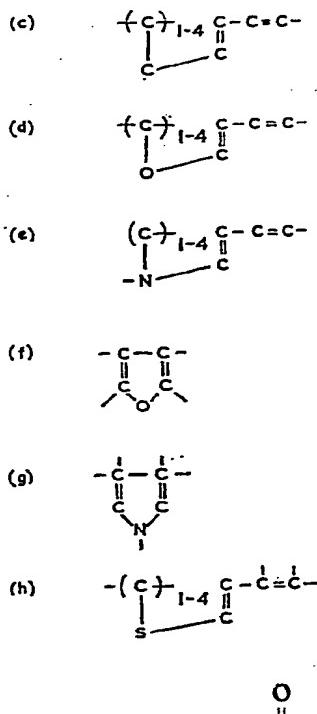
(A) at least one nickel salt;
(B) a brightener containing an acetylenic group;

(C) a sulfo-oxygen carrier;
and characterized by the presence therein of
(D) a water-soluble unsaturated tempering agent adapted to prevent misplating comprising a carboxylic acid, ester thereof or amide thereof, having one of the following nuclei

therein:

(a) —C≡C—

(b) —C=|C—C=C—C—



where the carbonyl radical $\text{---C}=\text{}$ of the carboxyl, ester or amide group is attached directly one of the above nuclei or through a methylene group to the nuclei. Groupings such as for example alkyl, aryl, amino, cyano, halo, hydroxyl and the like also may comprise part of the compounds.

The invention also consists in a process for nickel plating which comprises electrodepositing nickel on a base material from said bath.

The expression "water-soluble" when used in conjunction with the unsaturated acid esters and amides is intended to mean that compounds have sufficient water solubility to impart a tempering effect in overcoming misplating; usually the solubilities of water soluble tempering agents are in the range of from about 0.005 gram per liter to about 0.5 gram per liter or higher.

The invention is carried out advantageously by adding small amounts (less than 0.1 gram per liter) of at least one of the present tempering compounds to a nickel plating bath containing an active unsaturated brightener, prior to or during electrolysis of the bath. In many instances the unsaturated compounds, which may be used to overcome misplating, are also capable of functioning as brighteners with various degrees of effectiveness, and may be used in excess amounts, greater than 0.1 gram per liter, with no harmful effects to the deposit. Generally the effective amounts of the temper-

ing compounds differ from compound to compound, with the more effective or preferred compounds overcoming misplating at concentrations as low as 0.001 gram per liter or even lower. The less effective compounds are used effectively at higher concentrations, of an order 10 to 100 times the minimum effective concentrations necessary for the preferred compounds. Usually the unsaturated compounds show action in overcoming misplating before brightening action takes place or before deleterious effects to the plate are observed due to excessive amounts of the tempering agent.

The present invention provides a nickel electroplating bath and process, employing active acetylenic brighteners, for depositing brilliant, lustrous nickel plate on complex shaped articles free from misplate. The nickel deposits obtained through the practice of the present invention are not only of a superior brilliance and of substantially perfect continuity, but they also exhibit good to excellent ductility.

Specific compounds considered useful as brighteners of the second class include the water-soluble acetylenic compounds set forth in British Patent No. 747,098; the aryl, alkylenes and arylalkynoxy sulfonic acids set forth in U.S. Patent 2,800,442; the alkynoxy sulfonic and carboxylic acids having the triple bond separated from the acid radical by at least one oxygen atom set forth in U.S. Patent 2,841,602, and the unsaturated nitriles set forth in U.S. Patents 2,524,010 and 2,647,866.

The unsaturated carboxylic acids, esters and amides used as tempering agents to overcome misplating particularly are used with advantage in plating baths containing a Class I brightener (sulfo-oxygen compound) in addition to an unsaturated brightener (Class II).

These sulfo-oxygen compounds (Class I brighteners) generally comprise an aryl ring, a substituted aryl ring or an alkylenes chain with a sulfo-oxygen radical in the form of sulfonic acids, sulfonates, sulfonamides, sulfimides, sulfinic acid and sulfones. The aryl ring advantageously may be derived from benzene, naphthalene and the like, the substituted aryl ring may be derived from toluene, xylene, naphthylamine, toluidine, benzyl naphthalene and the like and the alkylenes chain may advantageously be derived from a vinyl compound or an allyl compound and the like.

The Class I brighteners (the organic sulfo-oxygen compounds) useful in carrying out the preferred mode of the present invention may advantageously be employed in similar amounts as the Class II brighteners. Generally it has been found, however, that the Class I brighteners should be present in amounts ranging from about 2.0 g./l. to about 5.0 g./l. In some instance amounts as high as 40 to 50 g./l. may advantageously be used.

Set forth in the following Table I are

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several compounds which show activity as Class II brighteners in acid nickel plating baths and the concentrations at which they brighten and also cause misplate and wherein the misplate was overcome using the present tempering agents.

TABLE I

| | Concentration at which misplating and brightening is observed grams per liter |
|--|---|
| (a) 1-Ethoxy-3-diethyl propargyl ammonium bromide propyne-1 | |
| $\begin{array}{c} \text{C}_2\text{H}_5 \\ \\ \text{HC}\equiv\text{CC}-\text{CH}_2-\overset{+}{\underset{\text{C}_2\text{H}_5}{\text{N}}}-\text{CH}_2-\text{C}\equiv\text{C}-\text{O}-\text{C}_2\text{H}_5 \\ \\ \text{Br}- \end{array}$ | 0.025 |
| (b) Bis(triallyl propargyl ammonium)—dimethyldichlorodibromostannate | 0.015 |
| $\left[\begin{array}{c} (\text{CH}_2=\text{CH}-\text{CH}_2)_3\text{C}\equiv\text{N} \\ \\ \text{HC}\equiv\text{C}-\text{CH}_2 \end{array} \right]_2 \left[(\text{CH}_3)_2\text{Sn Cl}_2 \text{ Br}_2 \right]$ | |
| (c) (1-Methoxy-1-pentene-3yne-5-dimethyl propargyl ammonium bromide | 0.02 |
| $\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3-\text{O}-\text{CH}=\text{CH}-\text{C}\equiv\text{C}-\text{CH}_2-\overset{+}{\underset{\text{CH}_3}{\text{N}}}-\text{CH}_2\text{C}\equiv\text{CH} \\ \\ \text{CH}_3 \quad \text{Br}- \end{array}$ | |
| (d) Diethyleneglycol monopropargyl ether | 0.008 |
| $\text{HC}\equiv\text{C}-\text{CH}_2-\text{O}-\text{CH}_2-\text{CH}_2-\text{O}-\text{CH}_2-\text{CH}_2-\text{OH}$ | |
| (e) Adduct of propargyl alcohol and 1,3-dioxolane | |
| $\text{HC}\equiv\text{C CH}_2\text{ O }(-\text{CH}_2\text{ O CH}_2\text{ CH}_2\text{ O})_n\text{ CH}_2\text{ O CH}_2\text{ OH}$ (supposed structure) | 0.01 |
| (f) Adduct of butynediol and 1,3-dioxolane | 0.05 |
| $\text{HOCH}_2\text{CH}_2\text{OCH}_2-(-\text{OCH}_2\text{CH}_2\text{CH}_2\text{OCH}_2)_n\text{OCH}_2\text{C}\equiv$ $\text{CCH}_2\text{O }(-\text{CH}_2\text{OCH}_2\text{CH}_2\text{O})_n\text{ CH}_2\text{OCH}_2\text{CH}_2\text{OH}$ (supposed structure) | |
| (g) 1-Ethynyl-1-cyclohexanol | 0.01 |
| $\begin{array}{c} \text{OH} \\ \\ \text{H}_2\text{C}-\text{C}\equiv\text{CH} \\ \\ \text{H}_2\text{C}-\text{CH}_2 \\ \\ \text{H}_2\text{C}-\text{CH}_2 \\ \\ \text{H}_2 \end{array}$ | |

TABLE I

Concentration at
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and brightening
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grams per liter

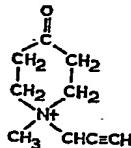
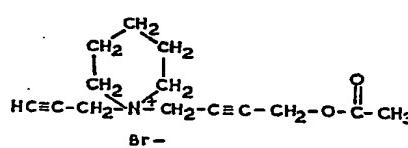
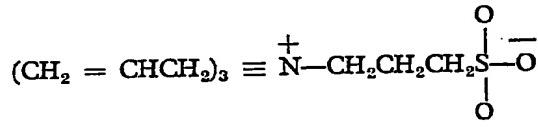
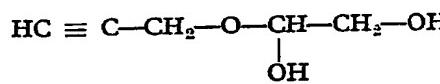
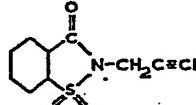
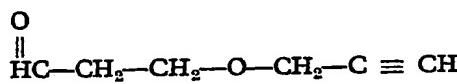
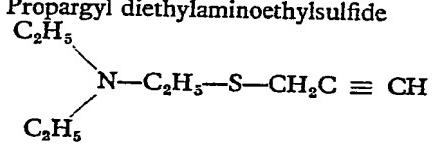
| | |
|--|-------|
| (h) 4-Keto-1-methyl-1-propargyl piperidinium bromide | 0.015 |
|  | |
| (i) 2-Butyne-1-acetoxy-4-piperidino propargyl ammonium bromide | .04 |
|  | |
| (j) Triallylammonium-γ-propane sulfonate | 0.25 |
|  | |
| (k) Monopropargylglyceryl ether | |
|  | 0.15 |
| (l) N-Propargylsaccharin | |
|  | 0.01 |
| (m) Beta-formylethylpropargyl ether | |
|  | 0.01 |

TABLE I

| | Concentration at which misplating and brightening is observed grams per liter |
|---|---|
| (n) Propargyl diethylaminoethylsulfide  | 0.2 |
| (o) Triallylamine $(\text{CH}_2 = \text{CHCH}_2)_3 \equiv \text{N}$ | 0.03 |
| (p) Butynediol $\text{HO}-\text{CH}_2-\text{C} \equiv \text{C}-\text{CH}_2-\text{OH}$ | 0.5 |
| (q) Propargyl alcohol $\text{HC} \equiv \text{C}-\text{CH}_2-\text{OH}$ | 0.01 |

- 5 The unsaturated brighteners, with or without a Class I brightener (sulfo-oxygen carrier), advantageously are used in bath solutions containing at least one of the following salts: nickel sulfate, nickel chloride, nickel fluoroborate and nickel sulfamate, wherein the solution is adjusted to an operating concentration of nickel. Included among the various baths useful with the present invention are (1) the various barrel plating baths generally comprising nickel sulfate and nickel chloride as the source of the nickel ion, and buffer systems comprising boric acid alone or in conjunction with magnesium sulfate or ammonium chloride, (2) the all-chloride bath designed for use where a high current density is desired, comprising nickel chloride as the source of nickel ion and boric acid as the buffer, (3) the fluoroborate bath comprising nickel fluoroborate as the source of nickel ion and free boric acid as the buffer alone or in combination with fluoroboric acid, (4) the common Watts-type bath designed for all purpose nickel plating and generally comprising nickel sulfate and nickel chloride as the source of nickel ion buffered with boric acid, (5) the all sulfamate bath comprising nickel sulfamate including boric acid as the buffer, and (6) the chloride-sulfamate bath comprising nickel chloride and nickel sulfamate with boric acid as the buffer.
- 10 The present invention is carried into effect
- 15 merely by adding one or more of the unsaturated compounds defined by formula I set forth below with one or more of the hereinbefore mentioned active acetylenic brighteners with one or more organic sulfo-oxygen compounds to an aqueous solution of one or more of the required nickel salts.
- 20 The resulting solution may be employed advantageously as an electroplating bath for the deposition of fully bright nickel using the same conditions substantially as are used for the basic bath without the tempering compounds. When employed with Watts-type, sulfamate or fluoroborate baths, the brightener systems, including the tempering agents of the present invention, provide a solution which can be operated effectively at current densities ranging from 10 to 200 amperes per square foot and preferably ranging from 25 to 100 amperes per square foot. The baths prepared according to the present invention may be operated at temperatures in the range of from 100°F. to 180°F. and preferably from 130°F. to 165°F.
- 25 In adjusting the composition of the nickel plating baths of the present invention, it is preferred that the resulting solution have a pH between 3.5 and 4.5. This pH range is however not critical; very satisfactory results are obtained from solutions having a pH value anywhere in the range of from 2 to 5.5. As
- 30

35 merely by adding one or more of the unsaturated compounds defined by formula I set forth below with one or more of the hereinbefore mentioned active acetylenic brighteners with one or more organic sulfo-oxygen compounds to an aqueous solution of one or more of the required nickel salts.

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- in most cases, the effective concentrations for each member of the class of compounds of formula I vary slightly and are partially dependent on the over-all bath composition and the plating conditions (temperature, current densities, etc.). The compounds defined by formula I are effective in amounts as low as .001 g./l. and may be used advantageously in amounts up to 0.1 g./l. Preferably the bath should contain at least 0.005 g./l. of a compound defined by formula I. Concentrations in excess of 0.1 g./l. tend to affect leveling slightly and provide no added advantage save the brightener effect previously mentioned.
- The present invention advantageously provides a bath and process useful in obtaining fully bright nickel at almost any thickness. The only criteria to be used in controlling the thickness are the cost of excessive nickel and the degree of ductility demanded. Maximum ductility is obtained at the minimum thicknesses required for obtaining a fully bright plate. Using baths prepared according to the present invention, a build-up of about 0.0001 to 0.0005 inch of nickel produces a highly ductile fully bright plate. Where a heavy plate is of primary concern, fully bright plates may be deposited to a thickness up to 0.1 inch or even higher. It is preferred, however, that the thickness of the nickel deposit be kept between 0.0002 inch and 0.01 inch. A nickel deposit having a thickness in this range is fully bright and ductile and provides the protection usually required for use in most environments.
- Nickel electroplating baths particularly useful in carrying out the present invention include the Watts-type and sulfamate type baths having increased nickel content. Such baths are designed for use with organic brighteners in general; they may be operated at the higher current densities desirable for the effective use of the present organic brighteners. For purposes of the present invention, the preferred Watts-type bath essentially comprises an overall nickel content ranging from 70 to 115 g./l. provided by 270 g./l. to about 450 g./l. of nickel sulfate and from about 20 g./l. to about 90 g./l. of nickel chloride with about 30 to 40 g./l. of boric acid as the buffer and the preferred sulfamate type bath essentially comprises an over-all nickel content ranging from 75 to 100 g./l. provided by nickel sulfamate with about 30 g./l. of boric acid as the buffer.
- For purposes of the present invention, boric acid is preferred as the buffer. Borax (sodium tetraborate), and other compounds commonly known to have utility as buffers, may be used with the baths of the present invention with no apparent undesirable effects.
- Illustrative examples of wetting agents which may be employed in the baths of the present invention include a great majority of the anionic surfactants. The sulfate type particularly may be used. Included among this type are the alkyl sulfates, aralkylsulfates, alkyl-

sulfonates, and the aralkylsulfonates.

The use of a wetting agent in baths prepared according to the present invention is optional; excellent deposits are obtained from baths having no wetting agent.

Illustrative examples of brighteners of the first class (the organic sulfo-oxygen compounds) to be employed as a co-brightener or cooperative addition agent of the present invention include the unsaturated aliphatic sulfonic acids, and alkali metal, ammonium, magnesium, and nickel salts thereof such as sodium vinyl sulfonate, sodium allyl sulfonate, diallylsulfone and the sodium salt of β -styrene sulfonate.

The aromatic sulfonic acids, and alkali metal, ammonium, magnesium, and nickel salts thereof such as benzene sulfonic acid, sodium benzene sulfonate, nickel benzene sulfonate, sodium p-toluene sulfonate, p-chlorobenzene sulfonic acid, sodium p-bromobenzene sulfonate, 1,2-dichlorobenzene sulfonic acid, sodium m-benzene disulfonate, nickel-m-benzene disulfonate, 1-amino-2,5-benzene sulfonic acid, o, m, and p-sulfonylbenzaldehyde, sulfonated naphthalene sulfone, 2-naphthalene sulfonic acid, 1,5- or 2,7-naphthalene disulfonic acid, nickel 1,5- or 2,7-naphthalene disulfonate, naphthalene trisulfonic acid, diphenyl p,p'-disulfonic acid, 2-naphthol-3,6-disulphonic acid and naphthylamine-3,6,8-trisulfonic acid.

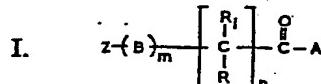
The heterocyclic sulfonic acids, and alkali metal, ammonium, magnesium, and nickel salts thereof including thiophene sulfonic acid, 2-(4-pyridyl) ethyl sulfonic acid and 2-(2-pyridyl) ethyl sulfonic acid,

The aromatic sulfonic acids, and alkali metal, ammonium, magnesium, and nickel salts thereof such as sodium benzene sulfinate, sodium p-toluene sulfinate and chlorobenzene sulfinic acid; and

The aromatic sulfonamides and sulfonimides such as benzenesulfonamide, p-toluenesulfonamide, saccharin, benzylsulfonamide, N,N-dimethyl-p-toluenesulfonamide, N,N-dicarboxyethyl benzenesulfonamide, dibenzenesulfonamide, p,p'-oxy-bis(dibenzenesulfonimide) or N,N-bis(phenylsulfonyl)-4,4'-biphenyl disulfonamide.

Additional sulfo-oxygen compound useful with the present invention include those disclosed in U.S. Patent 2,757,133 and British Patent No. 753728 which are incorporated herein by reference.

The water soluble unsaturated carboxylic acids, the esters thereof and the amides thereof may generally be represented by the general formula



- wherein m and n represent 0 or 1, A represents a radical selected from the group consisting of carboxyl, amido and ester radicals, B represents a radical selected from the group consisting of 5 $\text{C}\equiv\text{C}$ and $\text{C}=\text{C}$; Z and R represent $\begin{array}{c} | \\ \text{R}_3 \\ | \\ \text{R}_2 \end{array}$ to dodecyl; the substituted alkyl radicals also having from 1 to 12 carbon atoms such as the hydroxyalkyls including hydroxymethyl (carbinol), hydroxyethyl (methylcarbinol), to hydroxydodecyl, the haloalkyls having from 1 to 12 carbon atoms including halomethyl, haloethyl through halododecyl and the like (where halo can be fluoro, chloro, bromo or iodo), the carboxyl, carboalkoxy (esters) and amido alkyls having from 1 to 12 carbon atoms including carboxymethyl, carboxyethyl, carboxypropyl to carboxydodecyl, the corresponding carboalkoxy and amido derivatives; the nitroalkyls having from 1 to 12 carbon atoms including nitromethyl, nitroethyl to nitrododecyl and the like and the cyanoalkyls (nitriles) having 1 to 12 carbon atoms including cyanomethyl, cyanethyl to cyanododecyl; the alkenyl radicals having from 2 to 12 carbon atoms including ethenyl, propenyl to dodecenyl and the substituted alkenyls corresponding to the substituted alkyl analogues (supra) wherein each member of the alkenyl series is substituted with at least one radical from the group consisting of hydroxyl, fluoro, chloro, bromo, iodo, cyano, nitro, primary amino, secondary amino, tertiary amino, carboxyl, carboalkoxy and amido; the alkynyl radicals having from 2 to 12 carbon atoms including ethynyl propynyl to dodecynyl and the substituted alkynyls corresponding to the substituted alkyl analogue (supra) similarly as the substituted analogues; the aryl radicals including phenyl, naphthyl and anthryl; the substituted aryl radicals including the phenyl radicals having 1 to 5 and preferably 1 to 3 lower hydrocarbon radicals substituted thereon including methylphenyl (tolyl), ethenylphenyl, ethynylphenyl, pentylphenyl, pentenylphenyl, methylnaphthyl, ethylnaphthyl, ethynlynaphthyl, methyltolyl (dimethylphenyl), methylxyl (dimethyltolyl), pentyltolyl, pentylxyl, dimethylnaphthyl, pentylidimethylnaphthyl; the alpha, beta cycloalkenyl radicals having from 4 to 8 carbon atoms including alpha, beta cyclobutetyl, alpha, beta cyclopentenyl, alpha, beta cyclohexenyl, alpha, beta cycloheptenyl, alpha, beta cyclooctenyl; the unsaturated heterocyclic radicals containing nitrogen, oxygen or sulfur in the ring including furyl, thiophenyl, pyrrolyl, isopyrrolyl, oxazolyl, 1,2-pyranyl, 1,4-pyranyl, 1,2-pyronyl, indole acrylic acid, and wherein R₁, R₂ and R₃ represent the halo radicals such as fluoro, chloro, bromo and iodo and the same alkyl, alkenyl, and alkynyl and aryl radicals as are represented by Z.
- In formula I, Z can represent either a cycloalkenyl grouping or a heterocyclic radical containing nitrogen, oxygen or sulfur in the ring and having 4 to 8 carbon atoms. In this instance the ring must include at least two double bonds in a vinyl relationship with one another forming a conjugated system.
- Table II sets forth examples of the unsaturated compounds useful as tempering agents or additives in carrying out the present invention.
- wherein m and n represent 0 or 1, A represents a radical selected from the group consisting of carboxyl, amido and ester radicals, B represents a radical selected from the group consisting of 5 $\text{C}\equiv\text{C}$ and $\text{C}=\text{C}$; Z and R represent $\begin{array}{c} | \\ \text{R}_3 \\ | \\ \text{R}_2 \end{array}$
- a radical selected group consisting of hydrogen, hydroxyl, halo, cyano, nitro, carboxyl, carboalkoxy, amido, amino, monoalkylamino, dialkylamino, alkyl, cyanoalkyl, hydroxyalkyl, haloalkyl, carbamylalkyl, carboxyalkyl, nitroalkyl, aminoalkyl, monoalkylaminoalkyl, dialkylaminoalkyl, carboalkoxyalkyl, alkenyl, aralkenyl, cyanoalkenyl, hydroxyalkenyl, haloalkenyl, carbamylalkenyl, carboxyalkenyl, nitroalkenyl, aminoalkenyl, monalkylaminoalkenyl, dialkylaminoalkenyl, carboalkoxyalkynyl, alkenyl, aralkynyl, cyanoalkynyl, hydroxyalkynyl, carbamylalkynyl, carboxyalkynyl, nitroalkynyl, aminoalkynyl, monoalkylaminoalkynyl, dialkylaminoalkynyl, carboalkoxyalkynyl, aryl, alkaryl, alkenearyl, alkynaryl, nitroaryl, haloaryl, aminoaryl, alkylaminoaryl, carboxyaryl, amidoaryl, carboalkoxy, an alpha, beta cycloalkenyl group having 4 to 8 carbon atoms, unsaturated heterocyclic radicals containing nitrogen, oxygen or sulfur in the ring and having 4 to 8 carbon atoms, and R₁, R₂ and R₃ represent at least one member selected from the group consisting of hydrogen, hydroxyl, halo, alkyl, cyanoalkyl, hydroxyalkyl, haloalkyl, alkenyl, aralkenyl, cyanoalkenyl, hydroxyalkenyl, haloalkenyl, nitroalkenyl, alkynyl, aralkynyl, cyanoalkynyl, hydroxyalkynyl, haloalkynyl, nitroalkynyl, aryl, alkylaryl, alkenaryl, nitroaryl, and haloaryl.
- More specifically the compounds embraced by formula I include the carboxylic acids, the lower esters thereof and the corresponding carbamides wherein B represents an ethylenic radical ($\text{C}=\text{C}$) forming part of a conjugated system or an acetylenic radical ($\text{C}\equiv\text{C}$), wherein Z represents an olefinic radical or an unsaturated cycloaliphatic radical having at least one double bond in conjugation with the ethylenic radical represented by B; the compounds wherein Z represents the halo radicals such as fluoro, chloro, bromo and iodo, the amino radicals such as the primary amino radical, a secondary alkyl substituted amino radical such as monomethylamino, monoethylamino to monoctylamino, a secondary alkenyl substituted amino radical such as monoethenylamino, monopropenylamino to monoctenylamino, the secondary alkynyl amino radicals such as ethynylamino, propynylamino to octynylamino and the tertiary amino radicals having two of the corresponding alkyl, alkenyl and alkynyl radicals substituted directly on the nitrogen atom wherein each of the said radicals are the same or are different as to size or as to kind; the alkyl radicals, having from 1 to 12 carbon atoms including methyl, ethyl, propyl

tion, which when used in the plating bath in nickel electroplates having substantially no 5 conjunction with a brightener and preferably skipped or misplated areas. a sulfoxygen compound yield continuous

TABLE II

| | Effective grams amounts per liter | | | | | | | | | | |
|----------------------------------|--|---|---|--------------|---------------|----|----------------|----------------|----------------|---|---|
| | m | n | Z | A | B | R | R ₁ | R ₂ | R ₃ | | |
| (1) Propionic acid | | | | | | | | | | | |
| | .002 | 1 | 0 | H | | OH | $-C\equiv C-$ | | | | |
| (2) Phenylpropionic acid | | | | | | | | | | | |
| | .005 | 1 | 0 | | $-C\equiv C-$ | OH | $-C\equiv C-$ | | | | |
| (3) Phenylbutadiene malonic acid | | | | | | | | | | | |
| | .005 | 1 | 1 | | | OH | $-C\equiv C-$ | | H | H | H |
| (4) Sorbic acid | | | | | | | | | | | |
| | .02 | 1 | 0 | $CH_3CH=CH-$ | | OH | $-C\equiv C-$ | | H | H | |

TABLE II (Continued)

| | Effective gram amounts per litre | | | | | | A | B | R | R ₁ | R ₂ | R ₃ |
|-------------------------------------|---|---|---|--|------|---|---|---|----|----------------|----------------|----------------|
| | m | n | Z | | | | | | | | | |
| (5) Furic acid | | | | | 0 | 0 | | | | | | |
| (6) 4-Phenyl-3-butynoic acid | | | | | .005 | 1 | 1 | | H | H | | |
| (7) 5-Phenyl-2, 4-Pentadienoic acid | | | | | .005 | 1 | 0 | | OH | | H | H |

TABLE II (Continued)

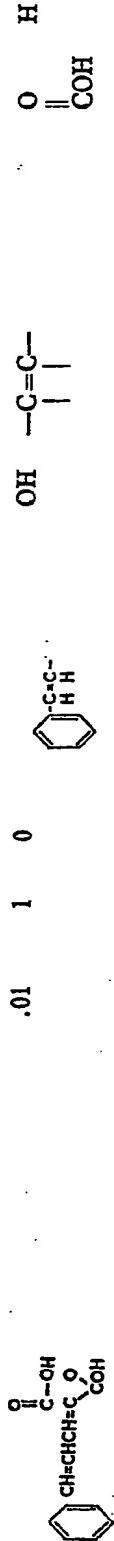
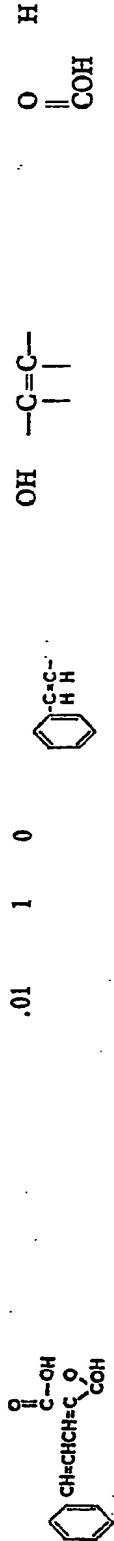
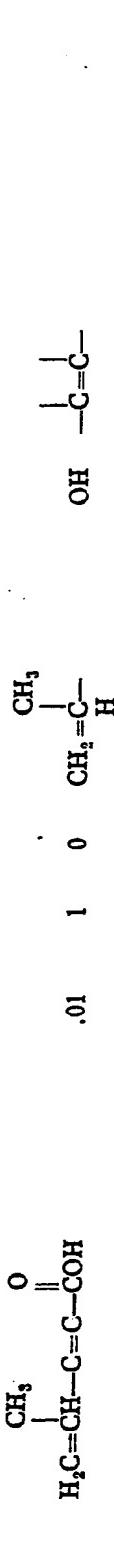
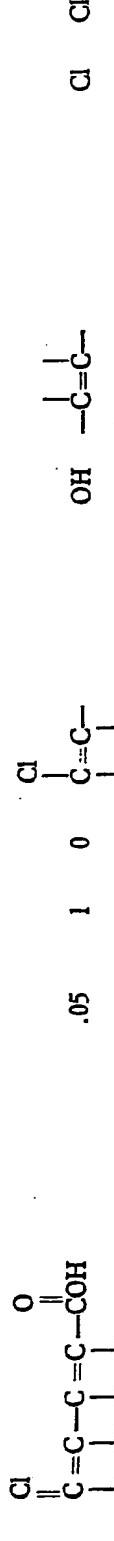
| | Effective gram amounts per liter | m | n | Z | A | B | R | R ₁ | R ₂ | R ₃ |
|--|---|---|---|--|--|--|----|--|---|----------------|
| (8) Cinnamalidene malonic acid | | | | | | | | | | |
|  | .01 | 1 | 0 |  | OH | $\begin{array}{c} \text{O} \\ \\ \text{C}=\text{C}- \end{array}$ | | | $\begin{array}{c} \text{O} \\ \\ \text{C}=\text{C}- \end{array}$ | H |
| (9) 4-Ene-4-methyl-2-pentyanoic acid | | | | | | | | | | |
|  | .01 | 1 | 0 | $\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_2=\text{C}=\text{C}-\text{C}-\text{COH} \end{array}$ | $\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_2=\text{C}=\text{C}-\text{C}-\text{COH} \end{array}$ | $\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_2=\text{C}=\text{C}-\text{C}-\text{COH} \end{array}$ | OH | $\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_2=\text{C}=\text{C}-\text{C}-\text{COH} \end{array}$ | | |
| (10) Pentachloro-cis-2,4-pentadienoic acid | | | | | | | | | | |
|  | .05 | 1 | 0 | $\begin{array}{c} \text{Cl} \\ \\ \text{Cl}-\text{C}=\text{C}=\text{C}-\text{COH} \\ \\ \text{Cl} \end{array}$ | $\begin{array}{c} \text{Cl} \\ \\ \text{Cl}-\text{C}=\text{C}=\text{C}-\text{COH} \\ \\ \text{Cl} \end{array}$ | $\begin{array}{c} \text{Cl} \\ \\ \text{Cl}-\text{C}=\text{C}=\text{C}-\text{COH} \\ \\ \text{Cl} \end{array}$ | OH | $\begin{array}{c} \text{Cl} \\ \\ \text{Cl}-\text{C}=\text{C}=\text{C}-\text{COH} \\ \\ \text{Cl} \end{array}$ | | Cl |

TABLE II (Continued)

| | Effective Gram amounts per liter | m | n | Z | A | B | R | R ₁ | R ₂ | R ₃ |
|---|---|---|---|---|----|---|---|----------------|----------------|----------------|
| (11) Furyl acrylic acid | | | | | | | | | | |
| <chem>CC(=O)C1=C(O)C=C(C=C1)C=C2C=CC(=O)C=C2</chem> | .05 | 1 | 0 | <chem>CC(=O)C1=C(O)C=C(C=C1)C=C2C=CC(=O)C=C2</chem> | OH | <chem>CC(=O)C1=C(O)C=C(C=C1)C=C2C=CC(=O)C=C2</chem> | H | H | | |
| (12) 1-Hydroxy-2-butyne-4-carboxylic acid | | | | | | | | | | |
| <chem>O=C(O)C#CC#C/C=C\O</chem> | .01 | 1 | 1 | <chem>O=C(O)C#CC#C/C=C\O</chem> | OH | <chem>O=C(O)C#CC#C/C=C\O</chem> | H | H | | |
| (13) Acetylene dicarboxylic acid | | | | | | | | | | |
| <chem>O=C(O)C#CC#C/C=C\O</chem> | 0.005 | 1 | 0 | <chem>O=C(O)C#CC#C/C=C\O</chem> | OH | <chem>O=C(O)C#CC#C/C=C\O</chem> | | | | |

The following examples are illustrative of the tempering effect of the unsaturated compounds useful in carrying out the present invention:

EXAMPLES I to VII
The basic bath composition (Watts type) used for all of the examples is set forth as follows:

| Components | Concentration grams per liter |
|--|----------------------------------|
| Nickel Sulfate | 300.0 |
| Nickel Chloride | 45.0 |
| Boric Acid | 41.25 |
| Wetting agent (2/3 dihexylester of sodium sulfosuccinate and 1/3 of sodium sulfate ester of 2-ethyl-1-hexanol) | 0.2 |

- 10 In each example different brighteners which cause misplating were added to this basic composition along with different Class I brighteners (sulfo-oxygen) carriers. The baths were adjusted to a pH of about 3.7 and electrolyzed at about 140°F. with air agitation. In each instance a nickel plate was deposited with and without the addition of an unsaturated compound (tempering agent) of the present invention.
- 15

20 **EXAMPLE I**
A bath solution having the above constituents plus two grams per liter of naphthalene disulfonic acid and 0.05 grams per liter of 1,3-dioxalane adduct of butyne diol was

25 electrolyzed using the above conditions and a current density of less than 40 amperes per square foot. The resulting deposit was bright with light haze and misplate in the recessed areas. Phenylpropiolamide (0.002 gram per

30 liter) was then added to the bath and another layer of nickel was deposited on another bent cathode. This nickel deposit was fully bright, was free from misplate or skipped areas.

- 35 Repeating the procedure substantially as outlined in Example I, nickel was electrodeposited on a bent cathode from a similar bath containing 2.5 grams per liter p,p'-oxybis(dibenzenesulfonimide) instead of the naphthalene disulfonic acid and 0.01 gram per liter of propargyl alcohol as the brightener. The current density employed was 40 amperes per square foot. The resulting deposit was only semi-bright with unplated or misplated sections in the recessed areas. Using the identical bath, an additional 0.02 gram per liter of propargyl alcohol was added along with 0.01 gram per liter of 4-ene-4-methyl-2-pentanoic acid. Nickel was again electrodeposited on a bent cathode at a current density of 40 amperes per square foot. The resulting deposit was considered fully bright and manifested no

misplating or skipped areas.

EXAMPLE III

Following the procedure substantially as outlined in Example I nickel was electrodeposited on a bent cathode from a bath containing 2 grams per liter saccharin and 1 gram per liter of alkylsulfonate in place of the naphthalene disulfonic acid and 0.015 gram per liter of 4 - keto - 1 - methyl - 1 - propargyl - piperidinium bromide as the brightener (Class II). The current density employed was 40 amperes per square foot. The resulting deposit on the bent cathode was only semi-bright, misplated with unplated sections in the recessed areas. 0.01 gram per liter of 1-hydroxy-2-butyne-4-carboxylic acid was added to the bath and nickel electrodeposited on a bent cathode. The resulting nickel deposit was obtained substantially free of misplated areas with no increase in brightness. Under the same conditions a fully bright and misplate-free deposit was obtained from the bath containing the carboxylic acid and an additional 0.02 gram per liter of 4-keto-1-methyl-1-propargyl piperidinium bromide.

EXAMPLE IV

Using the same bath and conditions used in Example I but with 0.016 gram per liter of diethylene glycol monopropargyl ether and 2.5 grams per liter of N,N-bis(phenylsulfonyl)-4,4'-bisbiphenyldisulfonamide substituted for naphthalene disulfonic acid was electrodeposited on a bent cathode at a current density below 40 amperes per square foot. The resulting deposit was semi-bright and manifested severe misplate in the areas of low current density. Another nickel layer was electrodeposited on a bent cathode from the same bath containing 0.005 gram per liter of 4-phenyl-3-butynoic acid. The resulting deposit comprised a continuous nickel layer free from misplating without an increase in brightness. Fully bright

deposits of nickel with no misplate or skipped areas were obtained from the bath by an additional 0.02 gram per liter of the diethylene glycol monopropargyl ether.

EXAMPLE V

To the basic bath composition of Examples 1 to 7 was added 1.6 gram per liter of naphthalene disulfonic acid, 1 gram per liter of alkyl sulfonate and 0.1 gram per liter of butyne diol as the brightener. Nickel was electrodeposited from this bath on a bent cathode at current densities of 40 amperes per square foot. The deposit had full brightness with fair levelling and no misplate or skipped areas. When an additional 0.05 gram per liter of butynediol was added to the bath, nickel electrodeposits could be obtained with improved leveling but misplating occurred in the recessed areas of a bent cathode where the current densities were below 5 amperes per square foot. 0.005 gram per liter of phenyl butadiene malonic acid then was added to the bath containing the additional butynediol and nickel was again electrodeposited on a bent cathode at the same current density. The resulting nickel deposit was fully bright, free from misplate and manifested excellent leveling characteristics.

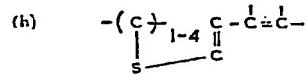
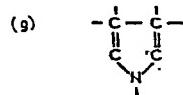
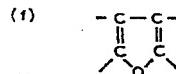
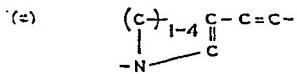
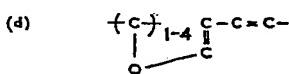
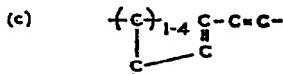
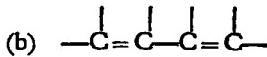
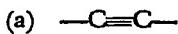
Although specific examples have been set forth hereinabove, it is not intended that the invention be limited solely thereto, but to include all of the variations and modifications falling within the scope of the appended claims.

WHAT WE CLAIM IS:—

- 35 1. A bath for electrodepositing bright nickel free of misplating comprising an aqueous solution of:
(A) at least one nickel salt;
(B) a brightener containing an acetylenic group;
(C) a sulfo-oxygen carrier;
and characterized by the presence therein of
(D) a water-soluble unsaturated tempering agent adapted to prevent misplating comprising a carboxylic acid ester thereof or amide thereof having one of the following nuclei therein:

40

45



wherein the carbonyl radical of the carboxylic acid, carboxylate ester or carboxylamide group is attached directly or through a methylene group to the said nuclei.

2. The bath according to claim 1 or 2 wherein said unsaturation of the tempering agent is provided by a radical having a conjugated system of double bonds.

3. A bath according to claim 1 or 2 wherein the brightening system includes diethylene glycol monopropargyl ether, N,N-bis phenylsulfonyl-4,4'-biphenyl disulfonamide, and 4-phenyl-3-butynoic acid.

4. The bath according to claim 1 or 2 wherein the brightening system includes the adduct of butynediol and 1,3-dioxolanone, naphthalene disulfonic acid and phenylpropiolamide.

5. The bath according to claim 1 or 2 wherein the brightening system includes 4-keto-1-methyl-1-propargyl pyridinium bromide, an alkyl sulphonate, and 1-hydroxy-2-butyne-4-carboxylic acid.

6. The bath according to claim 1 or 2 wherein the brightening system includes p,p'-oxy-bis-(dibenzenesulfonimide), propargyl alcohol and 4-ene-4-methyl-2-pentanoic acid.

7. The bath according to claims 1 or 2 wherein the brightening system includes naphthalene disulfonic acid, an alkyl sulphonate, butyne diol and phenyl butadiene malonic acid.

8. A process for nickel plating which comprises electrodepositing nickel on a base material from a bath according to claim 1 or 2.

9. A process for nickel plating which comprises electrodepositing nickel on a base material from a bath according to any of claims 1, 3 or 4.

10. A process for nickel plating which comprises electrodepositing nickel on a base material from a bath according to claim 5.

11. A process for nickel plating which comprises electrodepositing nickel on a base material from a bath according to claim 6.

12. A process for nickel plating which com- 95

prises electrodepositing nickel on a base material from a bath according to claim 7.

13. A process for nickel plating which comprises electrodepositing nickel on a base material from a bath according to claim 8.

14. A process for nickel plating which comprises electrodepositing nickel on a base material from a bath according to claim 9.

15. A process for nickel plating which comprises electrodepositing nickel on a base material from a bath according to claim 10.

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